

Effect of Filler Surface Treatment on Mechanical Properties and Thermal Properties of Single and Hybrid Filler-Filled PP Composites

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ABSTRACT: The influence of two types of surface treatments (aminosilane and Lica-12) on the mechanical and thermal properties of polypropylene (PP) filled with single and hybrid filler (silica and mica) was studied. An improvement in tensile properties and impact strength was found for both treatments compared to those of untreated composites. However, the filler with silane coupling agent showed better improvement compared to the

filler with Lica-12 coupling agent. This was due to better adhesion between filler and matrix. Thermal analysis indicates that surface treatments increased the nucleating ability of filler, but decreased the coefficient of thermal expansion of PP composites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 857–865, 2011

Key words: composites; fillers; mechanical properties; FTIR

INTRODUCTION

In recent years, there has been spectacular growth in the use of mineral filler in the plastics industry to improve specific properties or to reduce cost.¹ The use of talc as filler in polypropylene (PP) composites² by manufacturers has been growing since the 1980s, and today, talc plays a dominant role as the most widely used filler in PP composites. While newly developed additives, enhancers, and coupling agent may exist to enhance the properties of other composites using numerous different fillers, the use of talc as the main filler³ is still higher today as manufacturers have not lost their confidence in the good stability, process ability,^{4,5} and tensile properties of talc-filled PP. However, the use of talc has a trade-off in that talc is getting more costly, particularly for importing countries such as Malaysia, which lack sources of this material. The vast resources of silica, mica, and calcium carbonate in Malaysia have spurred many researchers and industries to switch to cheaper alternative fillers to fill PP composites. Previous works have reported such application mineral fillers, such as silica, mica, and calcium carbon-

ate, in thermoplastic composites.^{2–5} Studies on hybrid fillers in polymer composites are getting acceptance since they offer a range of properties that cannot be obtained with a single type of reinforcement. Various studies have been done on hybrid mineral filler-filled thermoplastic composites.^{6,7}

It is well-known that mineral fillers are hydrophilic; it is naturally not compatible with most polymers (e.g., PP) and must be chemically modified to render its surface more hydrophobic.^{4,5} One way of compatibilizing PP and inorganic filler is by modifying the filler surface, using coupling agents such as silane and titanate, and also by grafting small molecules such as acrylic acid, maleic anhydride, and acrylic esters onto the polyolefin chain.⁵ Silanes with different functional groups have been successfully applied for the treatment of filler in thermoplastic resin matrices.⁸ Silane coupling agents do not adsorb in a single layer on the filler surface, but form interphases with chemisorbed and physisorbed layers.^{8,9} The structure and composition of the interphases continuously change from the surface of the filler toward the polymer matrix. The subsequent layers of the silane form a network structure, which obviously influences the mechanical performance of the composites.¹⁰ The structure of the polysiloxane network can be affected by several factors such as the condition of the treatment (solvent, the concentration of the solution, and the pH of the aqueous slurry), the specific surface area of the filler, its chemical functionality, and the alkoxy- and organofunctionality of the silane.¹¹

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Demjan et al.¹⁰ have studied the effect of two aminofunctional silanes concentrated in PP/CaCO₃ composites; enhanced tensile strength and decreased deformability are observed in a treated system compared to that of a nontreated system. They also reported that an analysis of the interaction between silane coupling agent and CaCO₃ showed that aminofunctional silane adheres to the surface of the filler much stronger than other types of silane coupling agents. Dissolution experiment¹¹ proved that the adhesion between subsequent silane layers is as strong as the adhesion between the surface and the first layer, while in the absence of the amino group, the silane coupling agent could easily be dissolved from the surface of the filler.

Our previous work has been carried out to determine the mechanical and thermal properties of single fillers (mica, CaCO₃, and silica) and silica/mica hybrid fillers in PP composites.¹² It is observed that the tensile strength of single and hybrid filler composites without treatment decreased with the addition of filler owing to the incompatibility between hydrophilic fillers and hydrophobic matrix. Therefore, this study was carried out to improve the properties of single and hybrid fillers composites using two types of coupling agents. The influence of the surface treatment on the properties of single and hybrid fillers on PP was examined. The crystallization of hybrid composites was studied by differential scanning calorimetry (DSC), while the surface morphology of the samples was studied under scanning electron microscope (SEM).

EXPERIMENTAL

Materials

The homopolymer PP (Titanpro 6431) is a commercial product from Titan Polymer (M) Sdn. Bhd, with a melt index of 7 g/10 min and a density of 0.9 g/cm³. Silica and mica were obtained from Perak, Malaysia, and were finely grinded by using an Alpine 100 AFG opposed jet mill equipped with a 50 ATP-forced vortex classifier. The feed rate and grinding pressure were fixed constant at 12 kg/h and 6 bar, respectively, while the classifier rotational speed was fixed at 7000 rpm. The specifications of the fillers are shown in Table I. Here, two types of coupling agents were chosen to treat the mineral filler. The coupling agents were aminoethyl-amino-propyl-trimethoxysilane grade z-6020, supplied by Dow Corning (Singapore Pte Ltd), and neopentyl (diallyl)oxy, tri(dioctyl)phosphato titanate agent grade Lica-12, supplied by Kenrich Petrochemicals (Bayonne, NJ). The silane and titanate coupling agents were used as received.

TABLE I
Characterization of Mica and Silica Fillers

Sample	d_{50} (μm)	Span factor	Aspect ratio	Shape	Degree of crystallinity (%)
Mica	8.07	1.22	23.61	Flake	42.0
Silica	8.18	1.71	2.95	Elongated	73.6

Surface treatment

Silane treatment

In the first step, ethanol solutions (95% ethanol–5% water) were prepared by adjusting the pH between 3.5 and 4.5 with acetic acid, and then the silane was added while stirring. The silane loading to particulate mineral filler depends on the surface area of the filler and the coverage of the specific silane. In this study, all blends were prepared using 1 wt % silane coupling agent with respect to the filler. The solution was stirred for 10 min and then left for 1 h to allow for hydrolysis and silanol formation. Mineral filler was then added slowly and stirred continuously for another hour for further mixing. The treated mineral fillers were then dried at 110°C for 24 h to complete the evaporation of ethanol. The dried fillers were then rinsed again with ethanol to remove any residual silane before drying the filler again at the same temperature and for the same drying period. The treatment method based on the previous work by Leong¹³ was utilized in this study.

Titanate treatment

Toluene was used as a solvent to reduce the viscosity of the titanate. According to the previous work by Leong,¹³ the ratio of solvent to titanate was 3 : 1. The solvent and titanate were blended mechanically for ~ 30 min. The filler was then added and the slurry was mixed until good dispersion was achieved. The slurry was then dried at 80°C for 24 h. The filler was washed again with toluene to remove excess titanate and dried again at the same temperature and for the same drying period.

Sample preparation

The untreated and treated mineral fillers were dried in an oven at 100°C for 3 h to expel moisture prior to compounding with PP. The compounding of PP and untreated and treated mineral fillers was performed in two roll mill heaters. The PP compounds were prepared according to the various filler contents as indicated in Table II for untreated and treated filler. The temperature for both roll mills was set up at 180°C, and well-dried fillers were then carefully added into the melting PP. The mixing of PP and

TABLE II
Composite Formulations According to the Weight Percentage (wt %) of Each Component

Formulation	PP (wt %)	Mica (wt %)	Silica (wt %)
PP	100	0	0
S40	60	0	40
M10S30	60	10	30
M20S20	60	20	20
M30S10	60	30	10
M40	60	40	0

S and M refer to silica- and mica-filled PP, respectively.

mineral fillers was carried out for 15 min, followed by compression molding in an electrically heated hydraulic press at 180°C. Then subsequent cooling was carried out under a hydraulic pressure of 100 kg/cm³ for 3 min. Two similar series of single and hybrid filler-filled PP composites were prepared in the presence of silane and titanate coupling agents.

Testing and characterization

FTIR analyses were done for treated filler to determine the chemical structure before and after filler treatments. About 5 mg of filler was mixed with potassium bromide (KBr) prior to compacting into thin pellets with a hydraulic press using 400 psi of pressure and held for 3 min. The pellets were then inserted into Nicolet Avatar 360 FTIR spectrophotometer to be scanned using OMNics software. Void content was determined from the relationship between the theoretical density and the actual density of the composite. This test was performed according to ASTM D2734-94.

The crystallization behavior and melting characteristics of the composites were studied by DSC using a Perkin-Elmer DSC-6 in a nitrogen atmosphere at a heating and cooling rate of 20°C/min. In the first heating and cooling scans, the samples were heated from 50 to 220°C and held there for 1 min to eliminate the thermal history and cooled to room temperature at 20°C/min to record the crystallization behavior. A second heating was also performed similar to the first heating rate. The values of crystallization entropies (ΔH_c) were calculated from exothermic peak areas. The exothermic peak temperatures were taken as the crystallization temperature (T_c). The degree of crystallinity (DOC) was calculated from the heat of fusion by taking 207 J/g as enthalpy of perfect 100% homopolymer PP.¹⁴ The coefficient of thermal expansion (CTE) analysis was determined using a dilatometer at a heating rate of 5°C/min from room temperature to 125°C. The linear CTE $\alpha(T)$ was calculated on the basis of the following formula:

$$\alpha(T) = \left(\frac{\Delta L}{L}\right) \left(\frac{1}{\Delta T}\right)$$

where L is the sample's original length (at room temperature), T is the sample's temperature, and ΔL is the change in the sample's length owing to a change in its temperature (ΔT).

The tensile properties were measured using an Instron machine, according to ASTM D638. The crosshead speed of 5 mm/min was used in this testing. The unnotched Izod impact test was carried out, according to ASTM D256-02, using a Galdabini 1890 impact tester at an impact energy of 5.5 J. The dimensions of the samples for impact test were 12 × 3 × 60 mm³. For these two testings, the values reported were the average values of five specimens for each sample. The morphology of tensile fracture specimen was evaluated by ZEISS SUPRA 35 VP Field Emission SEM (FESEM).

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy

Fourier transforms infrared (FTIR) spectroscopy analyses were used for the detection of chemical reactions leading to chemical coupling of polymer and filler. The 4000–400 cm⁻¹ wave number range of the difference in the spectra of mica and silica filler treated with different coupling agents-filled PP composites are presented in Figures 1 and 2. As seen in figure, PP shows its characteristic peaks at 1450 cm⁻¹, from the symmetric stretching vibration of -C-H in CH₃; at 1375 cm⁻¹, from the symmetric bending vibration of CH₃; and at 1166, 972, 840, and 808 cm⁻¹, from the vibration rocking of CH₃ and -CH₂ and the stretching of CH-CH₂ and CH-CH₃.¹⁵

As shown in Table III, the Si-O absorption band, N-H absorption band, and C-N absorption band

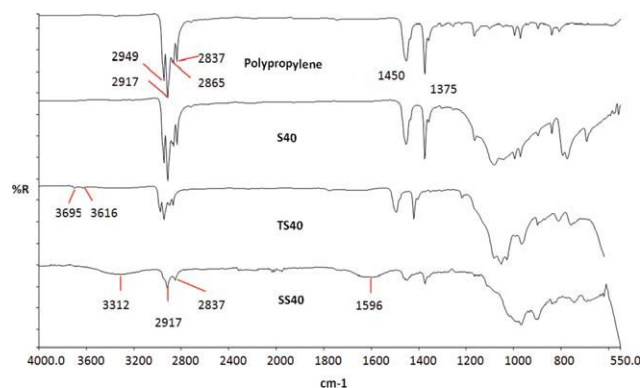


Figure 1 FTIR difference spectra of PP, untreated, and treated fillers composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

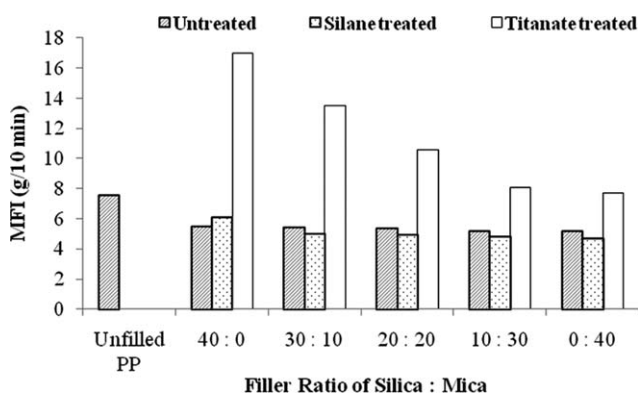


Figure 4 Effect of surface treatment on MFI of single and hybrid filler composite.

coupling agent has played a role in increasing the number of shorter polymer chains. This subsequently increases weight-average molecular weight (M_w) and decreases number-average molecular weight (M_n), which results in a broader MWD. In addition, according to Han et al.,¹⁶ the coupling agent might have diffused into the polymer matrix and acted as internal plasticizer, which could have increased the melt flow of the polymer phase. However, there were no significant effects on MFI for PP composites with silane coupling agent.

Tensile properties

The tensile strength and void content for PP/silica/mica hybrid composites with different filler ratios of untreated and treated filler are shown in Figure 5. It was observed that tensile strength increased with increasing mica content in PP/silica/mica hybrid composites. This is attributed to the nature of mica, which has high aspect ratios compared to silica, and this gives better surface contact area between filler and matrix in the PP/silica/mica hybrid composites. In general, all composites with surface-treated fillers increase their tensile strengths as compared to untreated filler composites. A previous work has reported that modification of composite with titanate and silane coupling agents improved the adhesion between the filler and the matrix; better dispersion and distribution were likewise exhibited in the matrix system.¹ According to Yazdani et al.,¹ treated filler with silane coupling agent forms a chemical bond between filler and matrix and consequently improves the dispersion of mica particles, their adhesion, and wetting, which lead to better phase interface and homogeneity in composites. Moreover, silane treatment creates a "protective layer," preventing the reagglomeration of the particles. Better adhesion and wetting are observed in the treated composites, hence creating fewer microvoids between filler and matrix. Demjan et al.¹⁰ studied

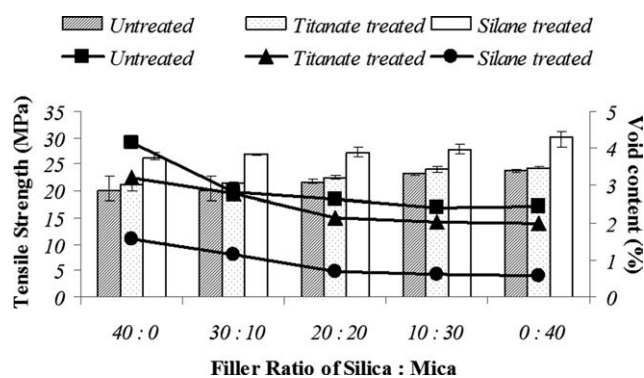


Figure 5 Effect of surface treatment on tensile strength and void content of single and hybrid filler composite.

the interaction between CaCO_3 and the eight silane coupling agents and found that the aminofunctional silane coupling agent showed a completely different behavior, which indicates that all layers are bonded strongly to each other. The very strong bonding of aminosilanes to the surface might be brought about by the catalytic effect of the amino group. Consequently, the silane condenses on the surface of the particles, forming a solid, solvent-resistant shell around them.⁸

The highest tensile strength was observed for the PP/mica compared to those containing silica. This could be due to high aspect ratio of mica particles, which leads to a good interfacial interaction with the polymer matrix. This subsequently facilitates a good stress transfer to the silicate layer and leads to improvement in tensile strength.¹⁶

Figure 6 shows the effect of surface treatment on the Young's modulus of PP/silica/mica hybrid composites. It can be seen that increasing the mica content into the PP matrix significantly increased its tensile modulus. The improvement in stiffness may be caused by the reinforcement effect of the rigid inorganic mica and the constraining effect of the silicate layer on the molecular motion of polymer molecular chain.^{18,19} According to Pukanszky,¹⁹ the Young's modulus was measured during the process of elastic

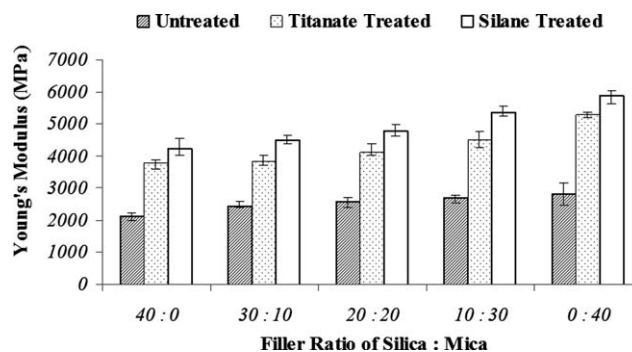


Figure 6 Effect of surface treatment on the Young's modulus of single and hybrid filler composite.

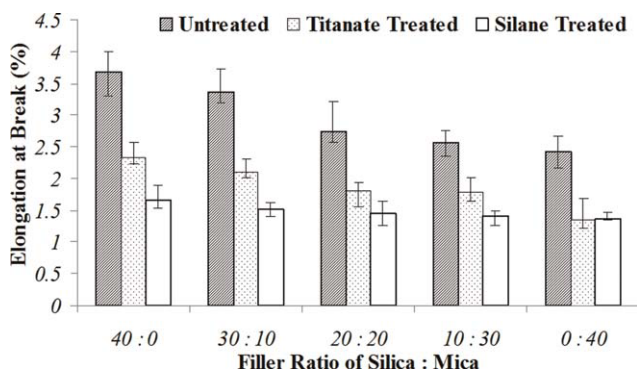


Figure 7 Effect of surface treatment on the elongation at break of PP/silica/mica hybrid composite.

deformation in the composites; the movements at the filler–matrix interfaces were very limited. In the polymer filled with rigid particles, the polymer itself solely contributed to the elasticity of the composites. Therefore, the modulus could not be used to characterize the strength of filler–matrix interactions, and so the value of the modulus should not have been affected even if strong filler–matrix interaction existed because of filler surface modification.

The three factors affecting the composites modulus were filler modulus, filler loading, and filler ratio. High-stiffness composites require filler particles of high modulus and high aspect ratio and preferably higher filler loading.⁵ The surface treatment of filler with titanate and silane coupling agents has led to a significant improvement of the Young's modulus in the composites, compared to untreated filler. This obvious result was due to the increase in the efficiency of perfect bonding between PP and filler, which consequently gave rise to a higher modulus.

The effect of surface treatment on elongation at break of PP/silica/mica hybrid composites is illustrated in Figure 7. Generally, adding a rigid particle into the PP matrix decreased the elongation at break. This may be due to restraints on the mobility of the

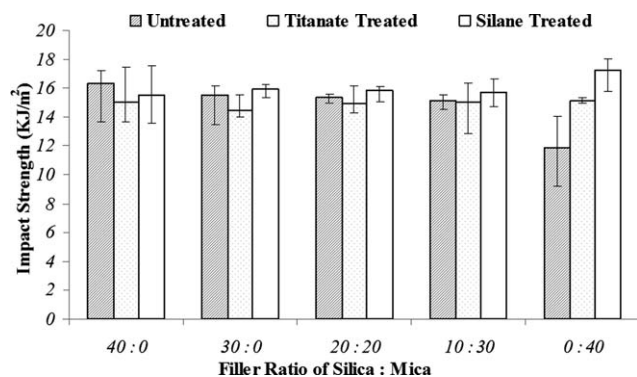


Figure 8 Effect of surface treatment on the impact strength of PP/silica/mica hybrid composite.

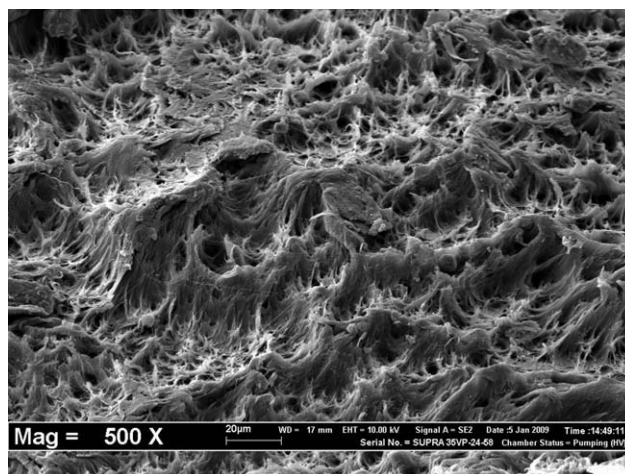


Figure 9 SEM micrograph of unfilled PP.

polymer chains caused by the intercalated filler.²⁰ From the figure, it can be seen that unfilled PP exhibits ductile failure, and the addition of filler results in immediate transition of deformation characteristic, that is, from ductile to brittle behavior.

Impact properties

Figure 8 demonstrates the effect of surface treatment on the impact strength of PP/silica/mica hybrid composites. The filler surface treatment with silane coupling agent results in good resistance to impact failure compared to untreated system. This effect is probably due to poor dispersion of untreated filler resulting from the higher particle–particle interaction. This means that the untreated particles will become more agglomerated, which will lead to more brittle behavior.

The surface fractures of unfilled PP, mica, and silica fillers, with or without surface treatment, were analyzed by SEM micrograph as shown in Figures 9–11. From the micrograph in Figure 9, it is obvious that the fracture behavior of unfilled PP was ductile. Ductile fracture is characterized by gross plastic deformation, as indicated by fibrillar structure. It has been observed that the untreated filler shows weak adhesion between filler and matrix. However, the particle distribution is good, which implies that an effective mixing had been accomplished.

Figures 10 and 11 show that surface treatment with silane and titanate coupling agents has improved the adhesion between filler and matrix. Much of the filler treated with silane coupling agent, which tends to be embedded inside the polymer matrix, is visible in this case. However, filler treated with titanate coupling agent tends to be exposed and loosely spread on the fracture surface, with some cavities surrounding the particles. This clearly indicates that filler/matrix interaction for filler with

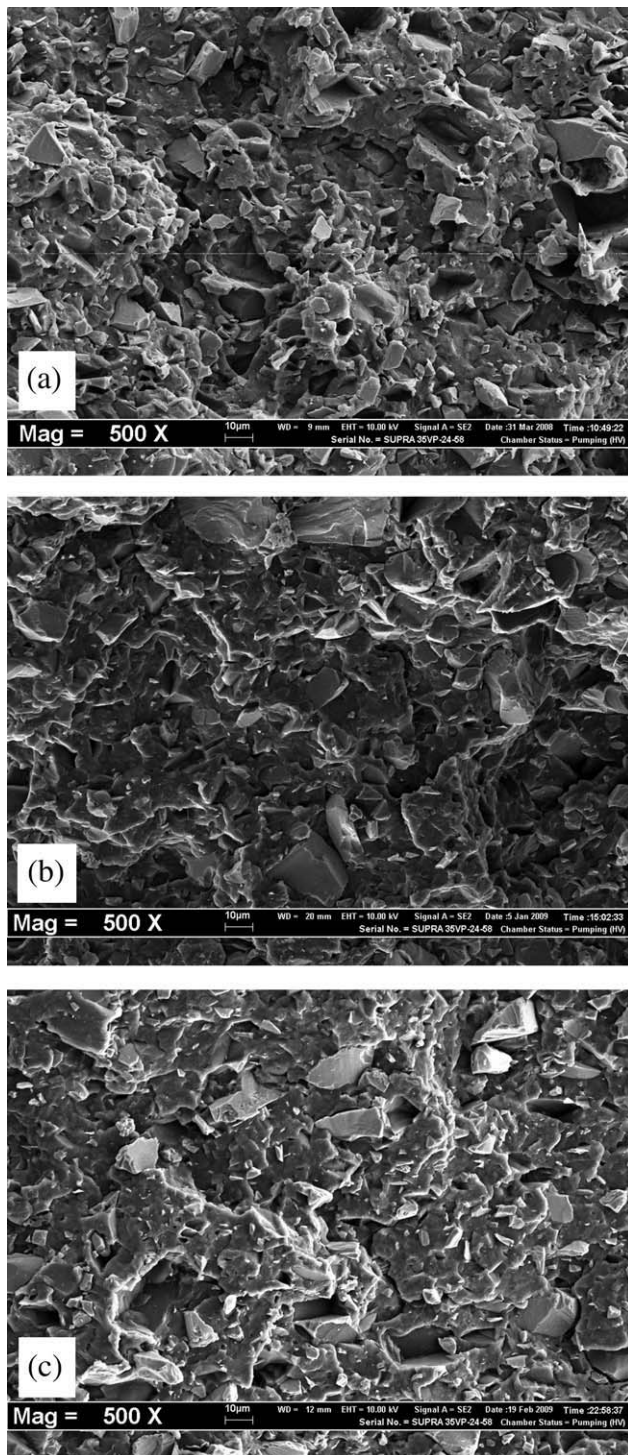


Figure 10 SEM micrograph of PP composites with (a) untreated silica, (b) silane-treated silica, and (c) titanate-treated silica.

silane treatment is better than that for filler with titanate treatment. According to Aboudzadeh et al.,²¹ the adhesion of filler treated with silane coupling agent in PP significantly increased, which was due to the change in the surface free energy and the generation of functional groups on the PP surface. They

also found that the better wetting of the surface by silane coupling agent was due to the reaction of oxygen with the PP surface which formed polar groups, therefore it can react with the silanol groups of the silanes. Functional groups of silane appeared on the

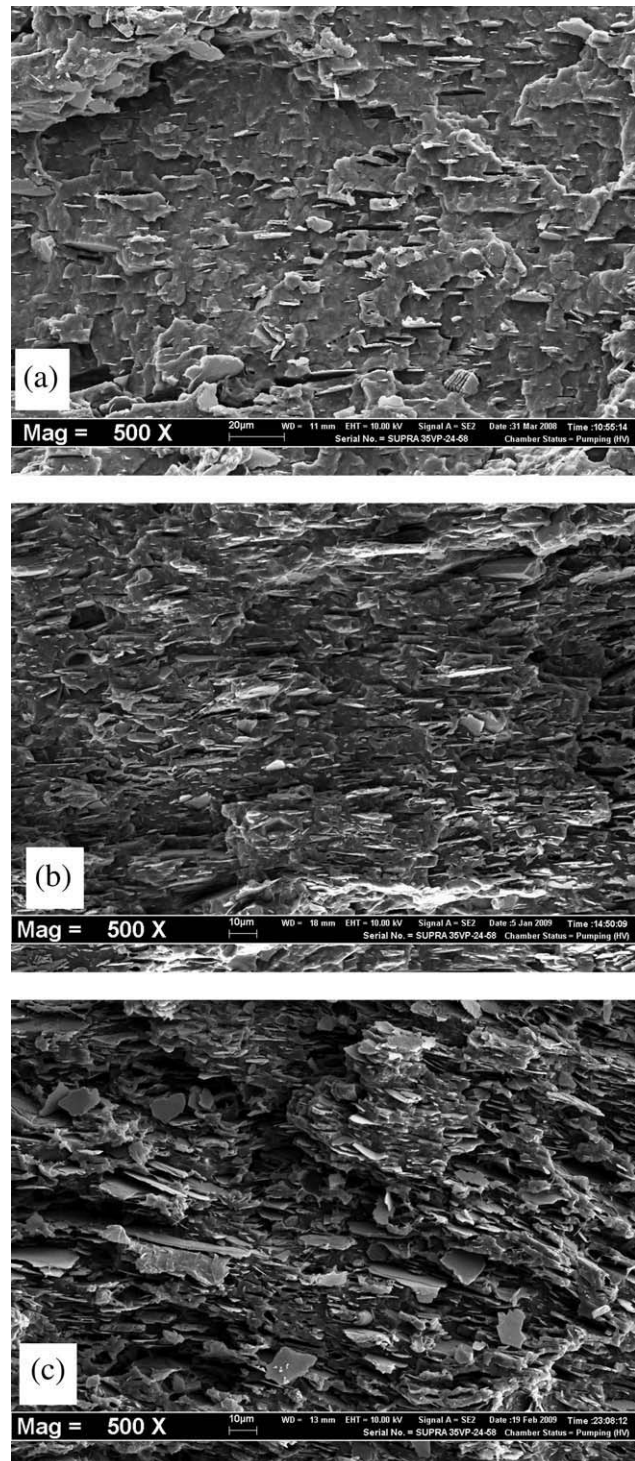


Figure 11 SEM micrograph of PP composites with (a) untreated mica, (b) silane-treated mica, and (c) titanate-treated mica.

surface of the fillers, which seem to be able to form chemical bond with the further applied coating.²¹

In general, it can be said that adhesion improved the mechanical properties for all treated filler composites, especially for the silane-treated filler. The improvement of adhesion also shows the decrease in the hydrophilicity of fillers through surface treatment, which makes fillers more compatible with the hydrophobic PP.²²

Thermal properties

The thermal properties of neat polymer, single filler, and hybrid filler composites with or without filler surface treatment were investigated via DSC. The crystallization temperature (T_c), crystallization entropies (ΔH_c), and DOC obtained from DSC studies are summarized in Table V. It is well-known that the presence of filler affects the crystalline structure of the PP.²³ The incorporation of mica and silica filler in PP composites increased the T_c , which indicates that these two fillers act as a nucleating agent. It was believed that the influence of viscosity increase on crystallization temperature overwhelmed that of the nucleation, which results in the lowered T_c .⁷

According to Pukanszky,¹⁹ the onset crystallization temperatures are proportional to the amount of crystalline phase. Nucleation increases the number of crystalline units, such as spherulites and lamellae, in the material, resulting in a decrease in their sizes. Monte²⁴ also cited that the titanate coupling agent would react with hydroxyl groups present at the filler surface to form a monomolecular layer that would increase the compatibility between the filler surface and matrix, thus improving filler dispersion. The change in crystalline structure could also possibly affect the properties of the composites, although other factors, such as particle orientation, could also play an important role.^{13,19} In addition, filler orientation and dispersion could affect the rearrangement and growth of crystalline units, where a good dispersion and improved particle orientation could

TABLE V
DSC Value of Unfilled PP and Single and Hybrid Filler-Filled PP Composites

Sample	T_c (°C)	ΔH_c (J/g)	DOC (%)
PP	113.809	-78.21	37.78
S40	117.122	-44.74	36.02
S20M20	117.067	-45.093	36.31
M40	119.124	-45.642	36.74
S-S40	119.730	-55.879	44.99
S-S20M20	119.742	-53.668	43.21
S-M40	118.401	-52.074	41.93
T-S40	118.430	-54.989	44.27
T-S20M20	119.083	-59.311	47.75
T-M40	118.439	-55.829	44.95

TABLE VI
CTE Value of Unfilled PP and Single and Hybrid Filler-Filled PP Composites

Sample	CTE (ppm/°C)
Unfilled PP	133.4
S40	99.65
M20S20	78.95
M40	67.19
S-S40	99.71
S-M20S20	73.06
S-M40	48.72
T-S40	85.17
T-M20S20	67.13
T-S40	54.79

reduce the hindrance of the particle to allow better spherulite growth and rearrangement.²⁵ Theoretically, the mechanical strength of a crystalline polymer is governed by its crystalline structure.

Table V also shows that titanate and silane coupling agents increase the DOC of the fillers and retard the motion of the PP chains.²⁰ This promotes the decrease of CTE composites with surface treatment as shown in Table VI. In many materials, the CTE values depend on the crystallographic direction along which it is measured. From the atomic perspective, thermal expansion is reflected by an increase in the average distance between the atoms.²⁶ As discussed before, the crystallinity of single and hybrid filler composite increases with the addition of silane and titanate coupling agents. This crystallinity effect then led to the change in CTE values of surface-treated composites. This is in agreement with previous work by Ahmad et al.²⁶ In addition, the CTE of the composites was not affected by the particles size and particle distribution of the filler. The CTE of mica and silica filler are 10 and 8 ppm/°C, respectively.

CONCLUSIONS

- The addition of silane and titanate coupling agents improves the interaction between fillers and PP, leading to a more effective transfer of the stresses from PP to fillers, thus increasing the tensile strength of the PP composites.
- Fillers treated with silane coupling agent show better tensile and impact properties compared to fillers treated with titanate coupling agent owing to the potential of silane to form a chemical bond between filler and matrix.
- The SEM micrograph reveals that the improvement in the mechanical properties of treated filler composites is largely contributed by the better adhesion between filler and matrix, which creates fewer microvoids in the treated filler

composites compared to the untreated filler composites.

- DSC data show that surface treatment improves the DOC of filler in PP composites, which leads to the increase in CTE value.

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